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SHORT COMMUNICATION

Measurement of the diffusivity of maleic acid by the rotating disc electrode technique

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1. Introduction

Diffusivity data for species reacting at an electrode–electrolyte interface are required for analysis of mass transfer phenomena. Predictive equations [1] applicable exclusively to binary electrolytic systems are not adequate for the calculation of diffusivity in multicomponent systems of practical importance. It is therefore necessary to experimentally determine diffusivity of the reactive species in such systems. Usually a diaphragm cell is used for measurement of molecular diffusivity in liquid media. The diffusion occurs through the pores of the diaphragm without accompanying physical or chemical interactions. However, in electrode processes, diffusion across the charged double layer is associated with chemical interactions such as protonation of reactive and intermediate species. These intermediate steps, along with charge transfer, are measures of the rate of the electrode reaction and the diffusion process under limiting current conditions. Therefore the diffusion coefficient measured by electrochemical methods is distinctly different from that measured using the conventional diaphragm cell. The former value could be termed as 'effective diffusion coefficient' and could be used in electrochemical systems.

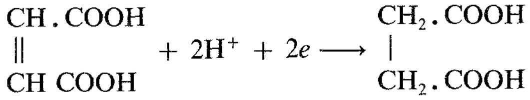
Among the various electrochemical techniques, the rotating disc electrode (RDE), because of certain advantages, has been widely used in the determination of diffusion coefficients in electrochemical systems [2, 3]. The RDE is one of the few cases for which an explicit solution to the Navier–Stokes equation is possible.

Levich [4] has obtained the solution of the convective–diffusion equation for the RDE by applying von Karman's hydrodynamic theory [5] and the solution is expressed in terms of limiting current density as follows:

$$i_L = 0.62408nFD^{2/3}\gamma^{-1/6}w^{1/2}C_b \qquad (1)$$

where i_L is limiting current density; n, the number of electrons participating in the reaction; D, the diffusivity of reactive species; γ, the viscosity of electrolyte, w, the angular speed of rotation and C_b, the concentration of reactive species in the bulk electrolyte. Equation 1 can be used directly for the experimental determination of diffusivity of the reactive species for known values of the other parameters.

The electrochemical reduction of maleic acid to succinic acid (represented by the following reaction) is an organic electrode process on a lead cathode without any side reaction in the prelimiting current region. The reaction involves protonation along with charge transfer and in a way is different from the metal dissolution/deposition reactions from simple plating baths.



$$\begin{array}{l}\mathrm{CH.COOH}\\ \Vert\\ \mathrm{CH\ COOH}\end{array} + 2\mathrm{H}^+ + 2e \longrightarrow \begin{array}{l}\mathrm{CH_2.COOH}\\ |\\ \mathrm{CH_2.COOH}\end{array}$$

2. Experimental details

The rotating disc electrode assembly has a conventional design. A brass rod of 5 mm diameter was embedded in a Teflon rod of outside diameter 10 mm. A lead disc cast on one end of the brass rod served as the working electrode. The working electrode was electrically connected to a potentiostat through a lead wire with a mercury pool contact. The assembly was

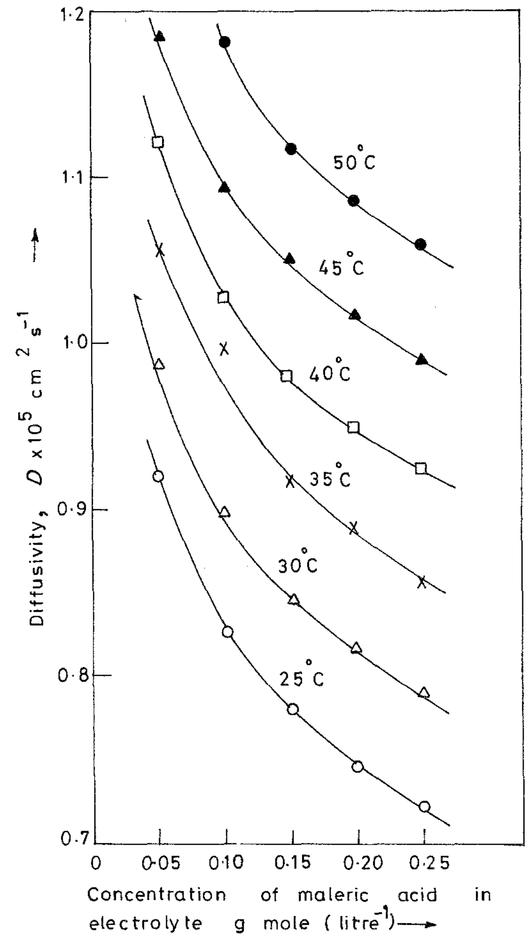


Fig. 1. Variation of diffusivity of maleic acid with bulk concentration.

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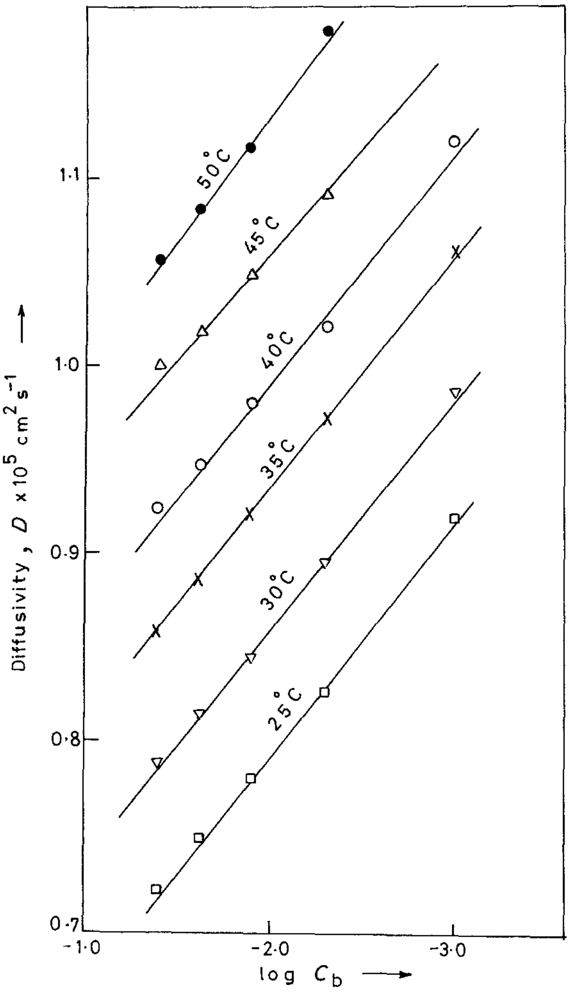

Fig. 2. Diffusivity vs log C_b plots.

driven by a synchronous motor connected through a set of pulleys and belts.

The electrolysis cell was a pear-shaped jacketted glass vessel with five openings and a capacity of 150 ml. The central opening was used to insert the rotating disc electrode assembly to the cell. The platinum counter electrode foil of size 5 mm × 5 mm was placed in the side arm of the cell. The electrolyte was maintained at the requisite temperature by circulating hot water through the cell jacket from a thermostatic bath.

Necessary polarization for the measurements was provided by a potentiostat. Current–potential curves were plotted with the help of an X–Y recorder (Ominographics-2000 Digilog). All the potential measurements were made with reference to a saturated calomel electrode and variation in current was measured as voltage drop across a known fixed resistor.

3. Results and discussion

Values of limiting current density, obtained from current–overpotential curves, were used to calculate the diffusion coefficient using the Levich Equation 1. The bulk concentration of maleic acid was varied from 0.05 to 0.5 M in a aqueous buffering mixtures of hydrochloric acid–potassium chloride (of concentration 2 M each). The temperature of the electrolyte was varied from 25 to 70° C. Polarization measurements were made at four rotation speeds of, viz. 430, 600, 750 and 950 rpm.

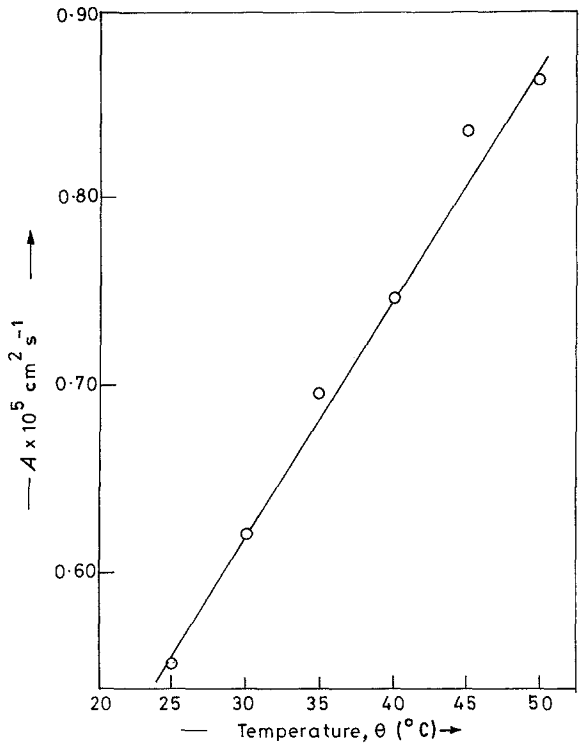

Fig. 3. Plot of intercepts from Fig. 2 vs temperature of bulk electrolyte.

Diffusion coefficients were plotted against molar bulk concentration of maleic acid with temperature as a parameter (Fig. 1). It is seen from Fig. 1 that diffusion coefficient decreases (logarithmically) with increase in the bulk concentration of maleic acid. Decrease in diffusion coefficients with increase in concentration has also been reported by Leffler and Cullen [6] for the non-electrolytic system methyl ethyl ketone–carbon tetrachloride, and by Gordon [7] for inorganic electrolytic systems of aqueous KCl, KNO_3 and NaCl solutions wherein minima were observed at specific concentration of the diffusing species. Ong *et al.* [8] have also reported a decrease in the diffusion coefficient with increase in concentration of *m*-nitrobenzene sulphonic acid in aqueous sulphuric acid medium.

In the present work attempts have been made to correlate diffusion coefficient with varying bulk concentration of maleic acid at different temperatures. With this aim, diffusion coefficients were plotted against logarithm of molar bulk concentration of the acid (Fig. 2) and the following empirical equation was obtained:

$$D \times 10^{-5} = A + B \log C_b \qquad (2)$$

where D is the diffusion coefficient of the reactive species in $cm^2 s^{-1}$. Constants A and B in the above equation are empirical in nature. The value of B has been observed to be invariant at -0.121, whereas that of A varied with temperature, in accordance with the following Equation 3 obtained from Fig. 3:

$$A = (0.248 + 0.0124\theta) \times 10^{-5}\,\mathrm{cm^2\,s^{-1}} \quad (3)$$

where θ is the temperature of the electrolyte in °C.

Under limiting current conditions, the concentration of reactive species varies in the vicinity of the electrode surface. At high bulk concentration of the species, the measured value is always an average of the local diffusion coefficient values existing through the diffusion layer. Acrivos [9] has shown that in such electrochemical systems one effective diffusion coefficient should prevail for mass transfer at limiting current even though the physical properties vary with composition in the diffusion layer. Newman [10] has also suggested the use of one *effective* or *integral* diffusion coefficient for describing mass transfer at limiting current which depends on bulk composition. With these considerations for comparatively higher concentration of reactant in electrolytes, it can be concluded that Equation 2 can be used for practical purposes in determining effective diffusion coefficients at different concentrations of maleic acid in the electrolyte.

4. Conclusions

Values of diffusion coefficients of maleic acid measured by the rotating disc techniques have been observed to decrease logarithmically with increase in the bulk concentration of maleic acid. The diffusivity data have been found to satisfy the proposed empirical equation which correlates diffusion coefficients with bulk concentration and temperature of electrolyte:

$$D = A + B \log C_b$$

where D is diffusivity in $\mathrm{cm^2\,s^{-1}}$, $B = 0.12 \times 10^{-5}$, $A = (0.248 + 0.124\theta) \times 10\,\mathrm{cm^2\,s^{-1}}$, θ is temperature in °C and C_b is bulk concentration in $\mathrm{mol\,dm^{-3}}$.

References

[1] T. K. Sherwood, R. L. Pigford and C. R. Wilke, 'Mass Transfer', McGraw-Hill Kogakusha Ltd, Tokyo (1975) p. 25.

[2] A. C. Ridiford, 'Advances in Electrochemistry and Electrochemical Engineering', edited by Paul Delahey, Wiley, New York (1966) Vol. 4, p. 47.

[3] Yu. V. Plesikov and V. Yu. Fillinovskii, 'Rotating Disc', Electrode Consultant Bureau, Plenum, New York (1976).

[4] V. G. Levich, 'Physicochemical Hydrodynamics', Prentice-Hall, Englewood Cliffs, New Jersey (1962).

[5] T. von Karman, *Z. Angnew. Math. Mech.* **1** (1965) 365.

[6] J. Leffler and H. T. Cullian, *Ind. Chem. Eng. Fund.* **9**(1970) 88.

[7] A. R. Gordon, *J. Chem. Phys.* **5** (1937) 522.

[8] J. Postlewaite, K. L. Ong and J. D. Pickett, *Can. J. Chem. Engng.* **50** (1972) 245.

[9] Andreas Acrivos, *The Physics of Fluids* **3** (1960) 657.

[10] John S. Newman, 'Electrochemical Systems', Prentice-Hall, Englewood Cliffs, New Jersey (1973) p. 272.